Some Unique Aspects of Mechanical Behavior of Metastable Transformative High Entropy Alloys

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This short review paper examines the uniqueness of metastable high entropy alloys (HEAs) that transform during plastic deformation. The linkages among alloy design induced metastablilty, processing induced "high enthalpy states" and evolving deformation micromechanisms are intriguing. One key aspect is the adaptive nature of deformation mechanisms because of activation of different micromechanisms during plasticity. This activation of deformation micromechanisms is attributed to transformation-induced plasticity in γ-f.c.c. phase and the evolving nature of c/a ratio in the ε-h.c.p. phase during deformation. As a result, metastable HEAs have good strength-ductility synergy and exceptional fatigue strength.

I. INTRODUCTION

METASTABLE HIGH-ENTROPY alloys (HEAs) have received attention by various research groups due to their excellent strength-ductility synergy at room temperature. Li et al.[1] introduced the concept of metastability to HEAs and reported first metastable HEA termed as dual phase HEA (DP-HEA) having a composition of $Fe_{50}Mn_{30}Co_{10}Cr_{10}$. The work was further extended by design of interstitial HEA ($Fe_{49.5}Mn_{30}Co_{10}Cr_{10}C_{0.5}$) by minor addition of carbon in DP-HEA to incorporate effect of precipitation strengthening along with classic transformation-induced plasticity (TRIP).[2] Formation of deformation twins was observed in equiatomic FeMnCoCrNi and $Al_xCoCrMnNi$ HEAs.[3–5] Addition of TRIP mechanism to HEAs extended the extent of deformation micromechanisms in HEAs which not only overcome the conventional strength-ductility tradeoff but expand the exceptional mechanical properties to fatigue and dynamic deformation.[3–5]

Our work on design of metastable HEAs by addition of Si in FeMnCoCr matrix further lowered the stacking fault energy.[6–9] We further modified these alloys with minor additions of Cu and Al.[10,11] These alloy design efforts impacted not only the high strength-ductility combination but also increased yield strength, fatigue limit and corrosion resistance.[6–12] We define the alloy design approach as *chemistry driven metastability*. In these alloys, the γ-f.c.c. phase transforms to the ε-h.c.p. phase and the stability of γ-f.c.c. phase can be tuned through alloy chemistry. Thus, depending on the composition, the starting microstructure at ambient temperature can be tailored from almost 100 pct γ-f.c.c. phase to near 100 pct ε-h.c.p. phase. It should be noted that the transition elements based HEA system such as Fe-Mn-Co-Cr-Ni have not exhibited the h.c.p. HEAs.[6–9]

Coupling the alloy design with friction stir processing, an innovative high temperature severe plastic deformation technique, opened up microstructural engineering pathways. An intriguing observation related to the change in the fraction of γ-f.c.c. and ε-h.c.p. phases in the starting microstructure based on processing parameters. We define this as *processing induced metastability*.[9] The change in grain size also impacts the metastability of the alloy during subsequent deformation. This has opened up the possibilities of exploring deformation mechanisms in somewhat unprecedented manner. The added complexities arise from (a) the evolving nature of c/a ratio in the ε-h.c.p. phase, and (b) the volume change during the γ-f.c.c. phase to ε-h.c.p. phase transformation. The origin of these observations is embedded in combined effect of alloy chemistry and prior processing. In this review paper, we propose that

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the combined effect of alloy chemistry and microstructural engineering can be captured better by the term, *high enthalpy states*. The metastability embedded in these high enthalpy states of HEAs influence the kinetics and extent of deformation induced transformation and subsequent twinning and/or c/a ratio evolution in the ε-h.c.p. phase.[6–13] The knowledge developed so far can be used to engineer a hierarchical progression of deformation mechanisms in these TRIP HEAs and this is conceptually discussed.

II. FRAMEWORK OF HIGH ENTHALPY STATES IN METASTABLE HIGH ENTROPY ALLOYS

Let us start with a temperature-pressure phase diagram[14] for pure iron (Figure 1(a)). Pure iron has four allotropic phases; α-Fe with b.c.c. crystal structure at low temperatures and pressures, γ-Fe with f.c.c. crystal structure at higher temperatures, δ-Fe with b.c.c. crystal structure at even higher temperatures, and at very high pressures (> 10 GPa), ε-Fe with h.c.p. crystal structure. This temperature-pressure diagram is explored at hydrostatic pressures. Relevant examples are obtained from high-pressure physics experiments carried out within diamond anvil cells, which restricts the exploration because of limited access to such facilities. The easiest experimental domain is the combination of ambient temperature and tensile/compressive stresses with deviatoric (shear) component up to ~2 GPa. This has historically excluded deformation studies on bulk ε-h.c.p. phase. Alloying approaches in iron have produced a vast array of steels with α-b.c.c. and γ-f.c.c. phases and a martensitic α′-b.c.t. phase.[15] The physical metallurgy of steels mostly revolves around the phase transformation from γ-f.c.c. phase to α′-b.c.t. and α-b.c.c. phases. The richness of steel metallurgy has led to twinning-induced plasticity (TWIP) and TRIP steels that exhibit attractive strength-ductility combinations.[15] But in all these years, investigation of plasticity in ε- h.c.p. phase was limited to its role in TRIP steels. Certainly, unlike ferritic, austenitic and martensitic

steels, there is no epsilon steel! Metastability engineered HEAs opened exploration of a new deformation-induced phase transformation domain that was otherwise unexplored in the conventional steels/alloys. It is interesting to visualize the equivalency with the large temperature-deviatoric stress region in Figure 1(a) with easier experimental access; through alloying, the metastable HEAs have condensed the temperature-deviatoric stress allotropic transformation domain for exploration of deformation-induced transformation of γ-f.c.c., ε-h.c.p. and α-b.c.c. phases in the easily accessible experimental regime of ambient temperature and conventional tensile/compressive testing stress ranges. Further, the stress required for deformation-induced transformation depends on the free energy difference, $\Delta G^{\gamma \to \varepsilon}$ at room temperature, and the threshold barrier for transformation. This concept is illustrated in Figure 1(b) for the Fe-Mn-Co-Cr-Si system. Before discussing the specific alloy system, a few generic observations are important. First, the relative positions of G^γ and G^ε in this example can be manipulated through alloy chemistry. Second, the threshold barrier for γ→ε transformation can be manipulated through processing and related microstructural changes. For example, introduction of high level of dislocations or grain boundaries in the γ-f.c.c. phase would increase the G^γ. This is depicted in Figure 1(b) as γ-f.c.c. phase with high enthalpy states. The basic thermodynamic considerations for HEAs was rooted in high entropy of mixing, ΔS_{mix}. For a given chemistry, the ΔS_{mix} for the solid solution γ-f.c.c. and ε-h.c.p. phases should be same. However, the additional role of ΔH because of stored dislocations and grain boundaries has not been discussed earlier.[15–17]

III. COMPOSITIONAL TAILORING OF METASTABLE HIGH ENTROPY ALLOYS

This short section highlights the conceptual illustration in Figures 1(b) and (c). Our initial work on metastable HEAs was built on the work of Li *et al.*[1]
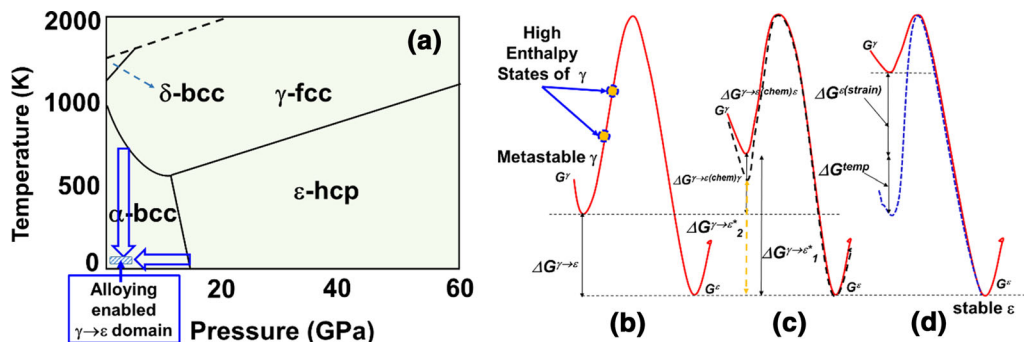

Fig. 1—(*a*) An illustration of the opportunity provided by high entropy alloys to shrink the temperature-pressure diagram to study the processing-induced and deformation-induced phase transformations at low temperatures and pressures. (*b* through *d*) Schematics showing the driving force ($\Delta G^{\gamma \to \varepsilon}$) for γ→ε transformation in FeMnCoCr matrix which can be manipulated by alloying (shift from (b) to (c)), and through deformation as in (d). The high enthalpy states can be introduced during processing through storage of high dislocation densities and boundaries. These high enthalpy states lower the threshold for transformation. (G^γ = free energy of formation for γ phase, G^ε = free energy of formation for γ phase, $\Delta G^{\gamma \to \varepsilon}$ (chem) = compositional contribution to the driving force, $\Delta G^{\gamma \to \varepsilon}$ (temp) = temperature contribution to the driving force, $\Delta G^{\gamma \to \varepsilon}$ (strain) = strain contribution to the driving force).

which pointed out that variation of Mn content at the expense of Fe content in the Fe-Mn-Co-Cr system can engineer γ-f.c.c. phase stability. Li *et al*.[1] further claimed that systematic decrease in Mn content to 30 at. pct resulted in the formation of γ-f.c.c. and ε-h.c.p. containing dual phase microstructure at room temperature. This was the first evidence towards the fact that the phase stability in Figure 1(b) can be influenced by proper selection of alloy chemistry in such a way that both γ and ε phases can be obtained by suppressing α-b.c.c. phase at room temperature. We extended this effort with a focus on making γ phase more metastable in Fe-Mn-Co-Cr matrix by (a) modification in alloy chemistry—as highlighted in this section, and (b) application of a high temperature severe plastic deformation technique (friction stir processing)—discussed in the next section. Earlier work on the TRIP assisted HEAs[16] and shape memory alloys showed that, addition of Co and Si can increase the driving force for the γ→ε transformation and thus we conducted thermodynamic simulations using ThermoClac TCHEA2 database predicting the $\Delta G^{\gamma \to \varepsilon}$ at room temperature for $Fe_{45-X}Mn_{20}Cr_{15}Co_{20}Si_x$ system to investigate the effect of Si addition in the presence of Co. Thermodynamic predictions showed that, Si addition in synergy with Co increases the driving force γ→ε transformation at room temperature in Fe-Mn-Co-Cr system.[16] This increased driving force is an indication of increased γ phase matrix metastability and thereby making extensive transformation to ε phase easier.

From the TRIP steel literature[15] we also understand that deformation storage capacity of γ matrix is also a crucial factor in deciding the propensity and kinetics of TRIP effect. Minor dissolution of γ phase stabilizers, such as Al or Cu, can increase its dislocation storage ability before it transforms to ε phase under stress. Fundamentally, increase in deformation storage ability is associated with delaying the formation of stable intrinsic stacking faults in the γ phase which later act as sites for the ε phase nucleation. To evaluate this, we also designed metastable HEAs with the minor addition of Cu or Al in $Fe_{40-X}Mn_{20}Co_{20}Cr_{15}Si_5Y_x$ (where Y is Cu or Al) system. Delayed TRIP effect in Fe-Mn-Co-Cr-Si matrix can be caused by decrease in the overall driving force $\Delta G^{\gamma \to \varepsilon}*_2$ (as shown schematically by the yellow dotted line in Figure 1(c)) due to addition of γ stabilizers like Cu or Al in comparison with higher driving force of $\Delta G^{\gamma \to \varepsilon}*_1$ (as shown schematically by the black dotted line in Figure 1(c)) in absence of those γ stabilizers.[15–18]

In short, metastability engineering through alloy design can condense the temperature-stress stability of γ phase to provide opportunities to study the γ to ε phase transformation at room temperature and conventional deviatoric stresses. This can be further extended to bring in the transformation to and from the α-b.c.c. phase at room temperature. Note that each of these transformations also involve volumetric changes that can be tuned through alloy design.[13–18]

IV. MICROSTRUCTURAL FLEXIBILITY: INTEGRATION OF ALLOY DESIGN WITH SEVERE PLASTIC DEFORMATION

Classic physical metallurgy is built on modifying microstructure to obtain desired properties. For example, an alloy is taken to high temperature to homogenize/solutionize and then quenched/cooled to low temperature. In $\alpha + \beta$ titanium alloys this will give the desired microstructure. If it is a precipitation strengthened alloy, the alloy is then aged to obtain desired final microstructure. Our use of the term "microstructural flexibility" for metastable TRIP HEAs is more nuanced. To understand this, let us compare heat treatment of Ti-6Al-4V alloy with friction stir processing of Ti-6Al-4V alloy.[19] The Ti-6Al-4V alloy undergoes allotropic transformation when cooled from the single-phase field above β transus. The microstructural response of just a thermal cycle (heat treatment) or a coupled thermo-mechanical cycle (friction stir processing) is similar other than concurrent grain refinement during the friction stir process. Change in the process parameters during friction stir processing, does not intrinsically change the phase stability of the α and β phases in this titanium alloy.[19] In contrast, when the TRIP HEA is friction stir processed, merely changing the tool rotation rate changes the phase fraction during cooling to ambient temperature. Therefore, each processing condition leads to a different final microstructure encompassing the phase fractions and the grain size. This broader range of microstructural space for the same alloy chemistry is *microstructural flexibility*.[8,9]

The responsive phase stabilization observed in the Si containing HEAs can be linked to increased metastability of the γ matrix. In metastable HEAs, the barrier for γ→ε transformation is dramatically reduced due to enhanced $\Delta G^{\gamma \to \varepsilon}$ and our conjecture is that simultaneous application of strain and temperature can create high enthalpy states (see Figure 1(b)) that alters the evolution of the ε phase during cooling from the processing temperature. To illustrate this processing-induced microstructural flexibility, Figure 2 shows the EBSD phase maps for Si containing HEAs in comparison with the dual phase HEA under various friction stir processing (FSP) conditions. Note that the higher tool rotation rate of 350 RPM causes higher temperature and higher strain/strain rate.[20] Figure 2 also includes examples of alloying effect. It is clear from Figures 2(a_1) through (c_1) that the phase stability is very sensitive to the alloy chemistry; which is obviously an expected response. Addition of Si leads to the dominance of ε phase at room temperature. Further, minor addition of Cu (1.5 at. pct) regained the dominance of γ phase in the microstructure under similar processing condition.

Figures 2(b_1) and (b_2, c_2) display the phase evolution in one of the Si containing HEA, namely $Fe_{40}Mn_{20}Co_{20}Cr_{15}Si_5$ HEA (CS-HEA), under different FSP processing conditions. It is clear that not only the alloy chemistry, but the processing condition can cause
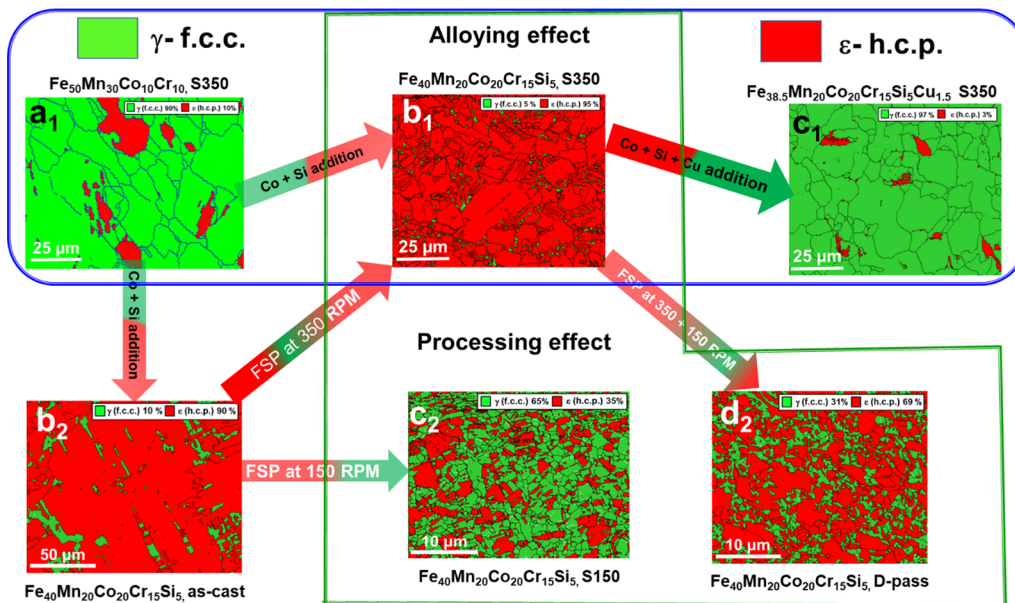
Fig. 2—EBSD phase map for (a_1) $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ HEA (DP-HEA), (b_1) $Fe_{40}Mn_{20}Co_{20}Cr_{15}Si_5$ HEA (CS-HEA), (c_1) $Fe_{38.5}Mn_{20}Co_{20}Cr_{15}Si_5Cu_{1.5}$ HEA (Cu-HEA) after FSP at 350 RPM, to illustrate the effect of alloy chemistry on stability of phases. EBSD phase map for CS-HEA in different processing conditions to highlight the effect of processing on phase stability, (b_2) as-cast, (b_1) single pass with tool rotation rate of 350 rpm, (c_2) single pass with tool rotation rate of 150 rpm, and (d_2) double pass with tool rotation rates of 350 rpm and 150 rpm.

sensitive phase stabilization as well. Higher RPM processing condition led to dominance of ε phase whereas low RPM processing led to formation of γ rich microstructure. Interestingly, combined processing with high and low RPM resulted in dual phase microstructure with higher fraction of ε phase.[9] Microstructurally, ε phase formation can be made easier if the density of stable stacking faults can be maximized which can be realized by minimizing the stacking fault energy (SFE). The SFE can be lowered in metastable HEAs by increasing the $\Delta G^{\gamma \to \varepsilon}$.[21]

V. MECHANICAL BEHAVIOR OF METASTABLE HIGH ENTROPY ALLOYS

The mechanical behavior of metastable HEAs can be altered by the metastability-linked SFE of the alloy and of course by changing the starting microstructure. As noted in the last section, the microstructural flexibility provides many different processing enabled variants to study the mechanical response. In a way, this escalate the vastness of possibilities; the enormous compositional possibilities of high entropy alloys is multiplied by the large number of microstructural variants for a given composition. In this illustrative example, Figure 3(a) shows the true stress-true strain curves for a few TRIP HEAs along with the work hardening rate (WHR). In spite of having different ε phase fraction (f_ε) and average grain size (d_{avg}) prior to deformation, all HEAs displayed ductility values greater than 25 pct and strength more than 1.1 GPa. Figure 3(b) shows true stress-true strain curves for one alloy (CS-HEA) under different

friction stir processed conditions. It is interesting to note that, the ductility is increasing with increasing strength in CS-HEA, thereby reversing the conventional strength-ductility trade-off paradigm. This is mainly attributed to hierarchical activation of deformation mechanisms as a function of prior d_{avg} and f_ε. It is also evident that all work hardening curves show regions of sustained work hardening rates over certain range of strain irrespective of alloy chemistry or processing condition (Figures 3(a) and (b)). The stress corresponding to the onset of sustained WH regime is termed as critical stress for TRIP and the strain range over which the WHR is sustained is called TRIP strain.[10–12,21] Another feature of these stress-strain curves is the lack of "non-uniform ductility". Conventional stress-strain curves of ductile materials have a region defined as uniform elongation, and there is a significant portion of non-uniform elongation. The non-uniform elongation part is responsible for necking and reduction of area. These TRIP HEAs on the other hand, show negligible non-uniform elongation. This is quite remarkable for alloys that have such high work hardening and very high overall elongation to failure. A simple interpretation of such failure is that the TRIP HEAs lack crack tip plasticity. Sinha et al.[22] showed that the fracture surfaces have shallow dimples, but obviously more research is needed to understand the details of fracture process in these alloys.

In order to understand the effect of prior d_{avg} and f_ε on deformation response in these metastable HEAs, TRIP stress is plotted with respect to ratio of f_ε and d_{avg} $\left(r = \frac{f_\varepsilon}{d_{avg}}\right)$ on log-log scale. It has been reported that
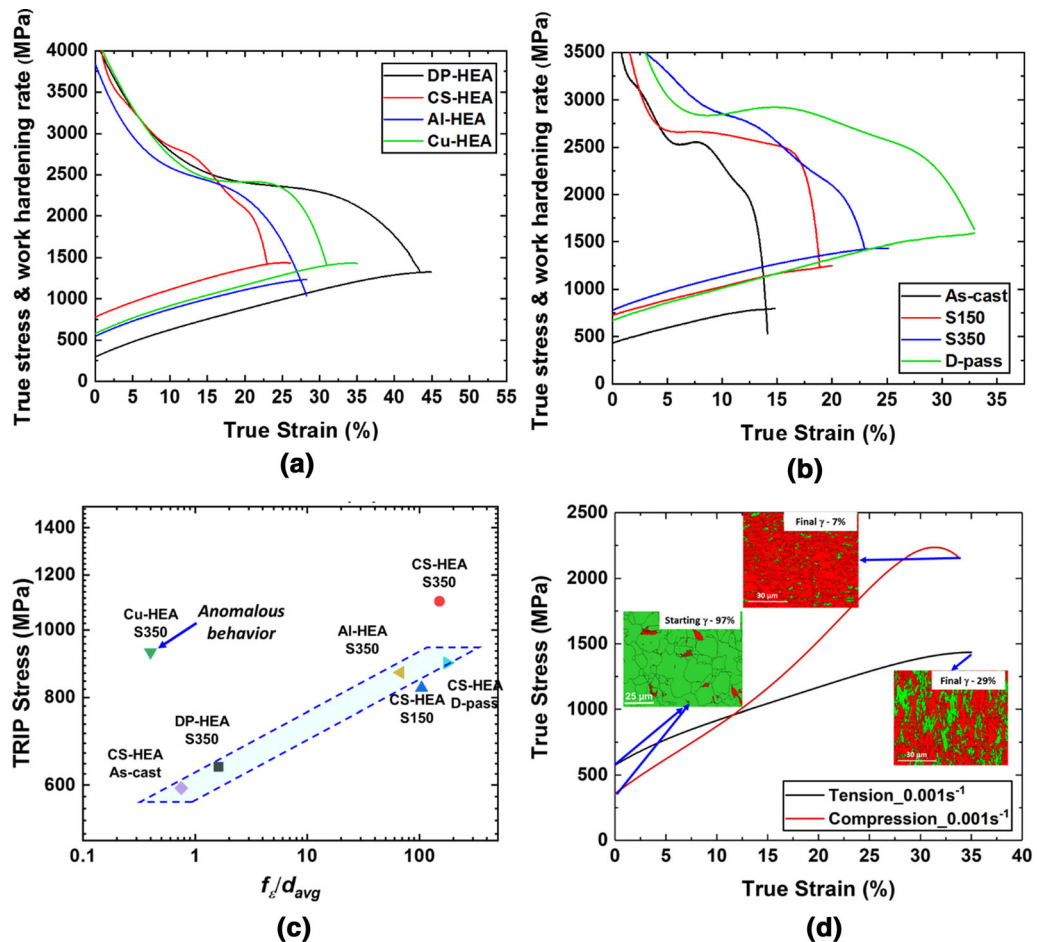
Fig. 3—(a) True stress-true strain curves with work hardening rate superimposed as a function of strain for all designed HEAs, (b) true stress-true strain curves with work hardening rate superimposed as a function of strain for CS-HEA under different FSP conditions, (c) TRIP stress *vs.* ratio of fraction of ε stabilized after processing to average grain size for all designed HEAs, and (d) comparison of tension-compression behavior of Cu-HEA after 350 RPM processing.

higher initial ε phase with very fine grain size (*i.e.* higher value of *r*) limits the TRIP effect, whereas coarse grained structure with marginal ε fraction enhances it.[1,6–8] In line with this expectation, the CS-HEA with highest *r* value showed highest TRIP stress whereas $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ HEA (DP-HEA) displayed lower r value with low TRIP stress (Figure 3(c)). However, $Fe_{38.5}Mn_{20}Co_{20}Cr_{15}Si_5Cu_{1.5}$ HEA (Cu-HEA) displayed anomalous behavior wherein it exhibited higher TRIP stress as compared to DP-HEA in spite of having lowest r value. This anomalous behavior of Cu-HEA raises the question about the impact of engineered γ metastability. What are the other factors governing the critical stress or strain required for the onset of γ phase transformation to ε phase? As discussed in a later section, the deformation of ε phase is quite complex as it involves evolution of *c/a* ratio and associated volume change. Additionally, the microstructural aspect comes out through comparison of as-cast material with friction stir processed conditions. The coarser grained as-cast material showed lower TRIP stress value in comparison to other fine-grained variants. Among the friction stir processed conditions, even though the r values are similar, the TRIP stress values are different. This

suggests that additional microstructural features or thermodynamic factors are needed to explain the TRIP stress values fully. The synergistic action of phase stability and processing conditions decides the activation of preferred deformation mechanisms and results in excellent strain hardening during deformation.[6–12,20,21] It is tempting to think about the effect of high enthalpy states on the onset of transformation. Critical experiments are needed to isolate each contribution to the TRIP stress and the extent of TRIP strain.

Figure 3(d) shows a comparison of stress-strain behavior in uniaxial tension and compression for the Cu-HEA that showed anomalously high TRIP stress in Figure 3(c). There are two striking aspects that we will like to highlight. First, the difference in the slope of stress-strain curves indicating significantly higher work hardening rate in compression. Second, for almost equal total plastic strain, the transformation of γ phase to ε phase is higher by >20 pct in the compression mode. As mentioned before, there is a negative volume change associated with γ phase to ε phase transformation. This result clearly shows that the stress state is an important factor for such transformative HEAs and the observations are quite different from conventional f.c.c. alloys,

like aluminum alloys, nickel alloys, copper alloys, and austenitic stainless steels. In conventional f.c.c. alloys, the stress-strain behavior in tension and compression are quite similar.[9–12,20–22]

The tension-compression asymmetry can have important implications for cyclic loading. A few fully reversible bending fatigue studies so far point to interesting research possibilities. Figure 4(a) shows the S-N curve of ultrafine grained Cu-HEA with very high endurance limit. In fact, a comparison with literature data for many different engineering alloys shows that the fatigue limit for this alloy, in both absolute value and UTS normalized value, are exceptional (Figure 4(b)). The origin of such high fatigue limit lies in γ phase to ε phase transformation at the crack tip (Figures 4(c,c_{1-3})).[12] There are three aspects to highlight here. First, the transformation of individual grains in a microstructure with randomly oriented grains. During tensile or compression test, a set of grains are favorably oriented for transformation. But during cyclic loading, the stress cycle reversal will add up the total activated grains in tension and compression. Second, let us consider the effect of grain size distribution on participation of overall volume during fatigue loading. In a conventional alloy, at any given fatigue stress, some fraction of grains in the microstructure will start deformation. This deformation percolates to other grains after hardening of initially weaker grains. The higher strain hardening rate of TRIP HEAs will lead to faster percolation of deformation to other grains. This will be aided by activation of different slip systems during tensile and compressive cycles. Third, the effect of volume change because of transformation. This is a bit complicated because the impact of volume reduction due to transformation will impact the tensile and compressive cycles differently. Intitutively, one can visualize that the volume reduction during γ phase to ε phase transformation will be aided by the compressive cycle. Quantification of these aspects is needed for TRIP HEAs with various level of metastability and starting microstructures.
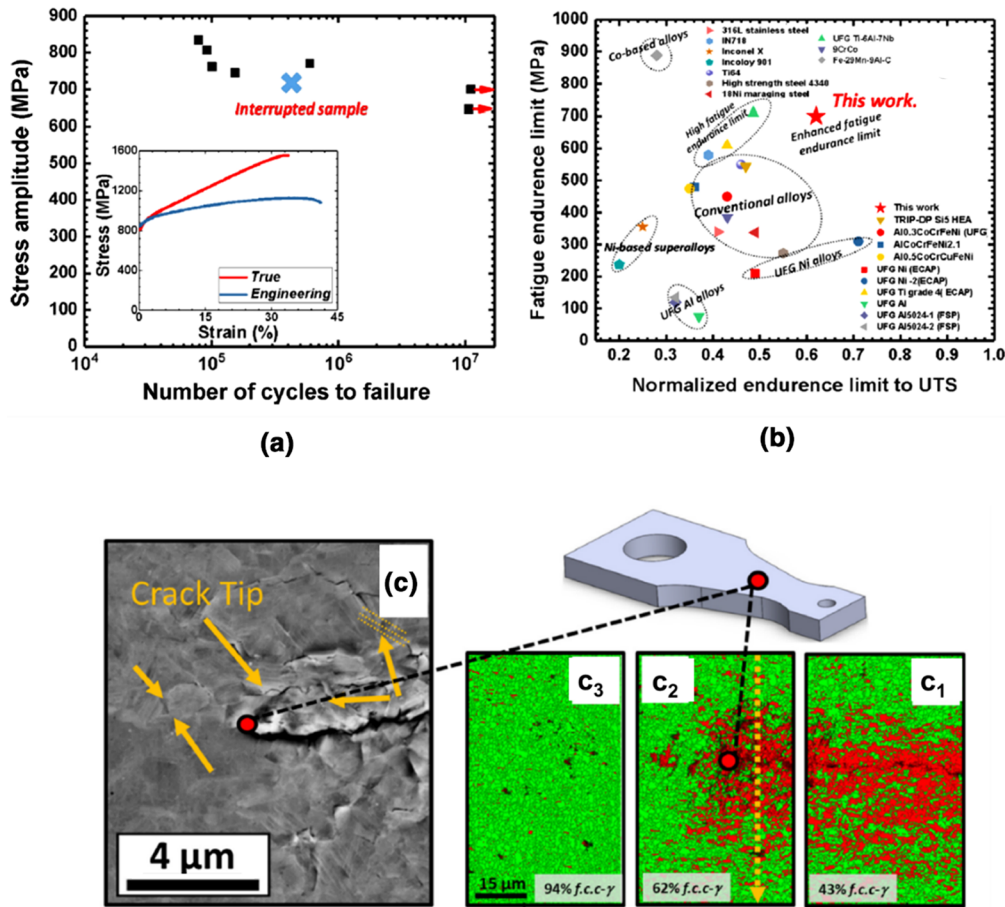

Fig. 4—(a) A S–N curve for ultrafine grained Cu-HEA,[12] (b) a plot of fatigue endurance limit vs. fatigue ratio comparing the ultrafine grained Cu-HEA with all other fatigue resistant materials,[12] and (c,c_{1-3}) EBSD phase map showing microstructural evolution along the crack and at the crack tip for an interrupted fatigue specimen at 114,710 cycles at 717 MPa (0.64 UTS).[12] Reprinted from Applied Materials Today, vol. 15, K. Liu, S.S. Nene, M. Frank, S. Sinha, R.S. Mishra, Extremely high fatigue resistance in an ultrafine grained high entropy alloy, 525-530, 2019, with permission from Elsevier.
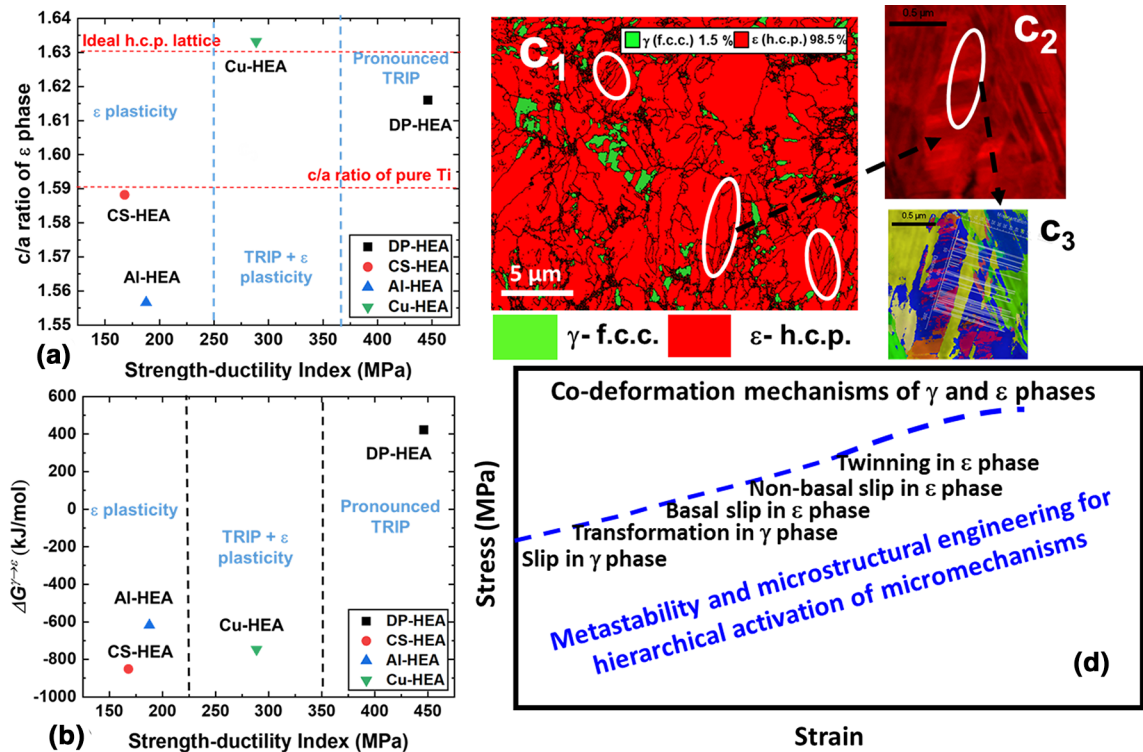
Fig. 5—(a) c/a ratio of ε phase as a function of strength-ductility index, (b) $\Delta G^{\gamma \rightarrow \varepsilon}$ value as a function of strength-ductility index of TRIP HEAs, (c_1) EBSD phase map for deformed specimen of CS-HEA, (c_2) PED phase map for as-deformed CS-HEA, (c_3) PED IPF map for as-deformed CS-HEA and (d) a conceptual stress-strain map of hierarchical activation of micromechanisms in TRIP HEAs.

VI. HIERARCHICAL ACTIVATION OF DEFORMATION MECHANISMS INCLUDING EVOLVING c/a RATIO

The TRIP HEAs discussed in this paper broadly show a progression of deformation mechanisms depending on the starting microstructure. The γ phase first deforms by slip, then transforms to the ε phase. The transformed ε phase, continues deformation through slip and twinning in the ε phase. A remarkable observation has been the evolution of c/a ratio in the ε phase during processing and subsequent deformation. This unique aspect of TRIP HEAs requires significant research to sort out the sequence of micromechanisms. In earlier studies on TWIP and TRIP steels, an understanding has emerged that the SFE of < 15-20 mJ/m^2 can induce TRIP effect whereas SFE > 20 mJ/m^2 effectively activates TWIP effect in the material. Frank et al.[6] have measured the SFE of CS-HEA to be ~ 6 mJ/m^2. This is quite low and tied with the evolution of micromechanisms observed in these TRIP HEAs. Metastable HEA alloy design approach provides an opportunity to fine tune the SFE of an alloy in such a manner that all these critical deformation mechanisms can become active hierarchically during the overall stress-strain response. This requires a deeper understanding of each micromechanism, including its dependence on thermodynamic and microstructural factors.[6-12]

Our earlier finding that the c/a ratio of ε phase in TRIP HEAs evolves with alloy chemistry, processing strain and subsequent deformation is scientifically quite intriguing and at this stage barely investigated. Figure 5(a) shows that, c/a ratio of ε phase varies between non-ideal value of 1.55 to ideal value of 1.633 depending on alloy chemistry for a given processing condition. However, all the HEAs exhibit strength-ductility index greater than 100 MPa suggesting higher work hardenability irrespective of c/a ratio. In h.c.p. alloys, the c/a ratio is considered critical in activation of twinning and non-basal $\langle c + a \rangle$ slip activities. Further, for a given h.c.p. alloy, the c/a ratio remains constant. The TRIP HEAs do show very significant non-basal slip activities which increase with strain. Figure 5(b) shows use of Thermo-Calc simulations for $\Delta G^{\gamma \rightarrow \varepsilon}$ and prediction of ε plasticity for CS-HEA and TRIP for DP-HEA This is further supported by the EBSD analysis of deformed microstructures. Figures 5(c_1-c_2) shows the presence of ε twins and plates in deformed CS-HEA specimen. The misorientation information between the matrix ε grain and the ε-twin was estimated with the PED IPF map shown in Figure 5(c_3) and found to be 58 deg corresponding to classical {10.1} contraction twinning. Thus, synergistic presence of non-plates and nano twins makes the ε dominated CS-HEA to accommodate higher strain after tensile deformation.[10,21-23]

Figure 5(d) attempts a conceptual wrap-up by listing of these micromechanisms. The overall deformation and fracture can be controlled by understanding and activating individual micromechanisms at particular trigger points. Both, thermodynamic aspects (to control the metastability) and microstructural aspects (to control the onset point and extent of individual micro-mechanism space) are important for the overall hierarchical activation of mechanisms. Such approach can be build to take full advantage of the vastness of high entropy alloy compositional space and microstructural control through innovative processes. Recently, Shukla et al.[22] have demonstrated the use of friction stir gradient alloying as a high throughput approach to explore such paradigm. The opportunities for fundamental research in this alloy design-processing-microstructure-mechanical properties space is limitless.[23]

VII. CONCLUDING REMARKS

The metastable high entropy alloys that exhibit deformation-induced phase transformation show some very unique mechanical behavior. Different micromechanisms get triggered during the stress-strain response of these alloys. Combination of alloy design to manipulate stacking fault energy and innovative processing steps to activate different high enthalpy states allows for exciting scientific opportunities. The γ-f.c.c. to ε-h.c.p. phase transformation is accompanied by volume change and the c/a ratio of the ε-h.c.p. phase evolves during processing and deformation. These features make the stress-strain response dependent on stress-state. Activation of different set of micromechanisms under tension and compression enables unique fatigue response with crack-tip transformation. Understanding of these micromechanisms will provide opportunities to co-design metastable alloy chemistry and microstructure to enable hierarchical sequencing of mechanisms to take fullest advantage of the potential offered by TRIP HEAs. New high throughput techniques like friction stir gradient alloying can be coupled with microscale testing to advance the scientific understanding at a faster pace.

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